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DIFFERENT PHASES OF DIFFERENTLY HEAT TREATED CdO FROM X-RAY AND TEM STUDIES

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Abstract: Differently heat-treated varieties of CdO, a typical IIB-VIA semiconductor, with interestingly different colours, have not been systematically studied earlier. The associated microstructural and lattice structural changes have been studied in the present work by transmission electron microscopy and x-ray diffraction, respectively, with additional chracterization of the observed defect structures by DTA-TGA techniques. These observations explain the extra lines in the XRD pattern that disappear at higher temperatures.

Keywords: CdO, defect structure, x-ray diffraction, TEM, DTA-TGA.

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1. Introduction

Binary AB type oxides, metallic and non-metallic, occupy a major and interesting position in materials science. While most oxides are insulators or bad conductors, a few binary and many multication oxides have been shown to be [1,2] electrically conducting, some being even superconducting at lower temperatures. Although some IIB-VIA semiconductors have been widely investigated [3] with respect to their band structures as well as electronic applications and these compounds (including CdO, the most ionic IIB-VIA compound) are well known for decades, there seems to be no systematic record and investigation of the different forms of CdO as obtained by different heat treatments [4].

There are a few early [4] records: brown CdO powder was obtained by burning Cd, and heating $Cd(OH)_2$ at around 350°C and 800°C resulted in two other varieties of CdO, including the 800°C black form. The colour changes have generally been attributed [4] to either defects in the NaCl-type lattice or to differences in particle size. As no detailed investigation has been reported in the literature to support these conjectures, TEM, XRD and DTA-TGA studies have been carried out in the present work. We have tried to generate these forms starting from available CdO by heat-treatment at 350°C and 800°C. Here an attempt has been made to correlate different x-ray diffraction patterns, not reported earlier, for differently heat-treated CdO samples to the results of thermogravimetric analysis, TGA, and differential thermal analysis, DTA.

2. Experimental Details

As-supplied samples of CdO (99.7%) with yellowish brown colour were subjected to stepwise heat treatment in a furnace with Eurotherm temperature controller for 36 hours initially at 350°C to achieve the above-mentioned colour change. As the formation of a deep brown or coffee brown variety was partial, the firing temperature was raised in steps. Firing the as-supplied powder at 400°C for 36 hours transformed the powder completely to the deep brown variety. Following the earlier literature another firing of the as-supplied powder at 800°C for 36 hours was carried out. This gave a black powder.

X-ray diffraction patterns for as-supplied and differently heat treated (at 125°C, 400°C and 800°C) samples have been taken and compared with the available standard pattern, representative patterns being shown in Fig.1.

Thermal Analysis in a standard DTA-TGA set-up has been carried out to investigate the possible loss/gain in weight and nature of thermal changes (Fig.2).

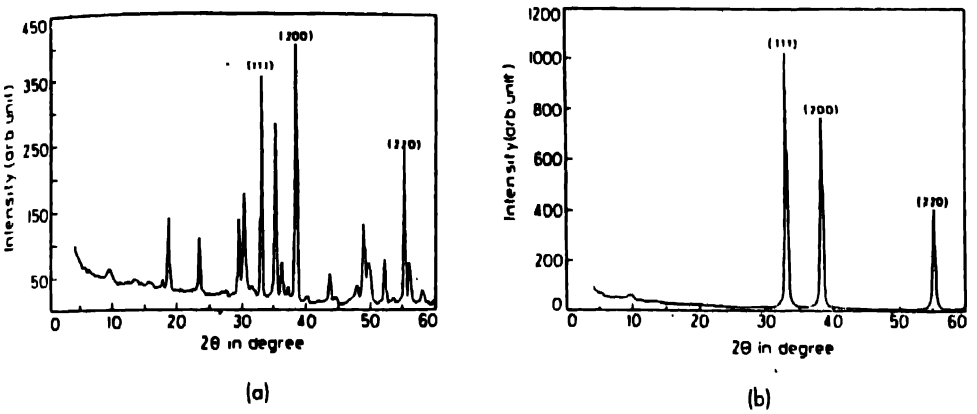

Fig.1. X-ray Powder Diffraction Pattern of (a) as-supplied CdO and (b) after our 400°C heat treatment. Pattern (b) , that also represents the XRD patterns for heat treatments at higher temeperatures, matches the JCPDS pattern.

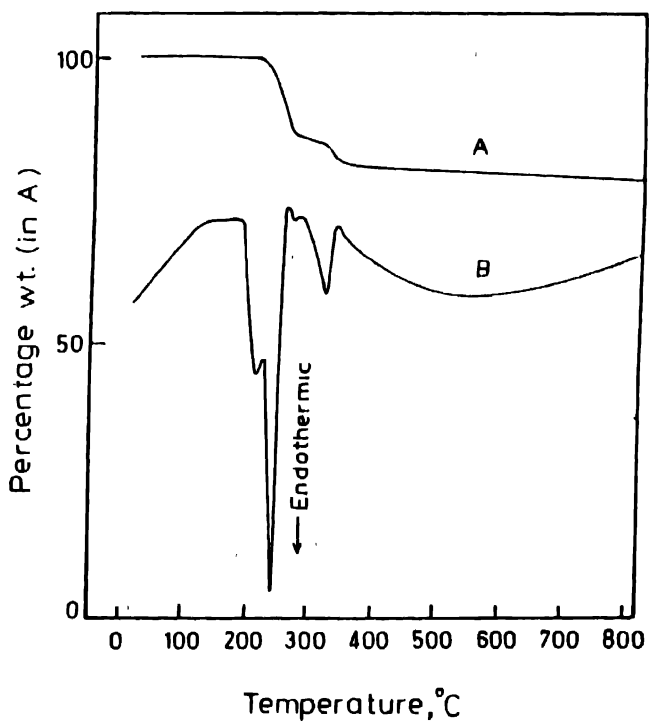

Fig.2. TGA (plot A) and DTA (plot B) results for CdO heated in air, to show its weight loss and associated endothermic dips.

The microstructure of the different forms has been investigated with Transmission Electron Microscopy (Fig.3). Electron diffraction patterns (mostly with 160 kV beam) and micrographs of different zones of the sample have been taken. The sample for electron microscopy was prepared by collecting its finely ground powder on a carbon grid from a suspension in ethanol, prepared by ultrasonic agitation. No change was observed in the microstructure with change of the solvent.

The resistivity was measured at room temperature by four probe method. The sample showed gradual decrease of electrical resistivity with increasing heat-treatment temperature, the decrease being about three orders of magnitude for the 800°C treatment.

3. Results and Discussion

Some authors [5] feel that it is chemically more correct to represent CdO as $Cd_{1+x}O$ to indicate that, like its nearest neighbour, ZnO, it contains excess metal ion in interstitial positions in its rocksalt lattice structure. The bonding is predominantly ionic in nature (as is reflected in the high value of the lattice energy, leading to a high melting point of 1700°C). Still the filled 4d orbital in CdO must have a role in determining the electrical properties. It is also probable that if allowed by symmetry, 4d orbital in Cd can hybridize with O(2p)-like states generating a net repulsion between the bands by virtue of which the valence band is shifted [3] towards higher energy side. Reduction of such repulsion by structural reorganization may lead to a reduction of electrical resistivity as has been observed in this present work. Neither the detailed structural data nor any calculation in this direction being available, the present aim is to clarify the structural changes as the first step of the work.

CdO is expected to have a standard rocksalt structure (JCPDS-ICDD and Philips XRD File) with (111) giving 100% intensity. The powder diffraction pattern of our as-received CdO reveals some extra lines in addition to the standard lines in the samples that we checked. The pattern matches the standard pattern only after our 400°C and higher temperature firings (Fig.1).

The DTA-TGA (Fig.2) gives a strong clue towards identifying the origin of these extra lines: the endothermic dips in the DTA graph corresponds to the multistep weight loss in the TGA plot. Repeated experiment showed that although the weight loss in various steps varies with a proportional change in the depth of endothermic dips from sample to sample, the tempratures of the steps and the nature of the plot remains the same. This weight loss, which starts at around 190°C and ends at 380°C, is to be attributed to the

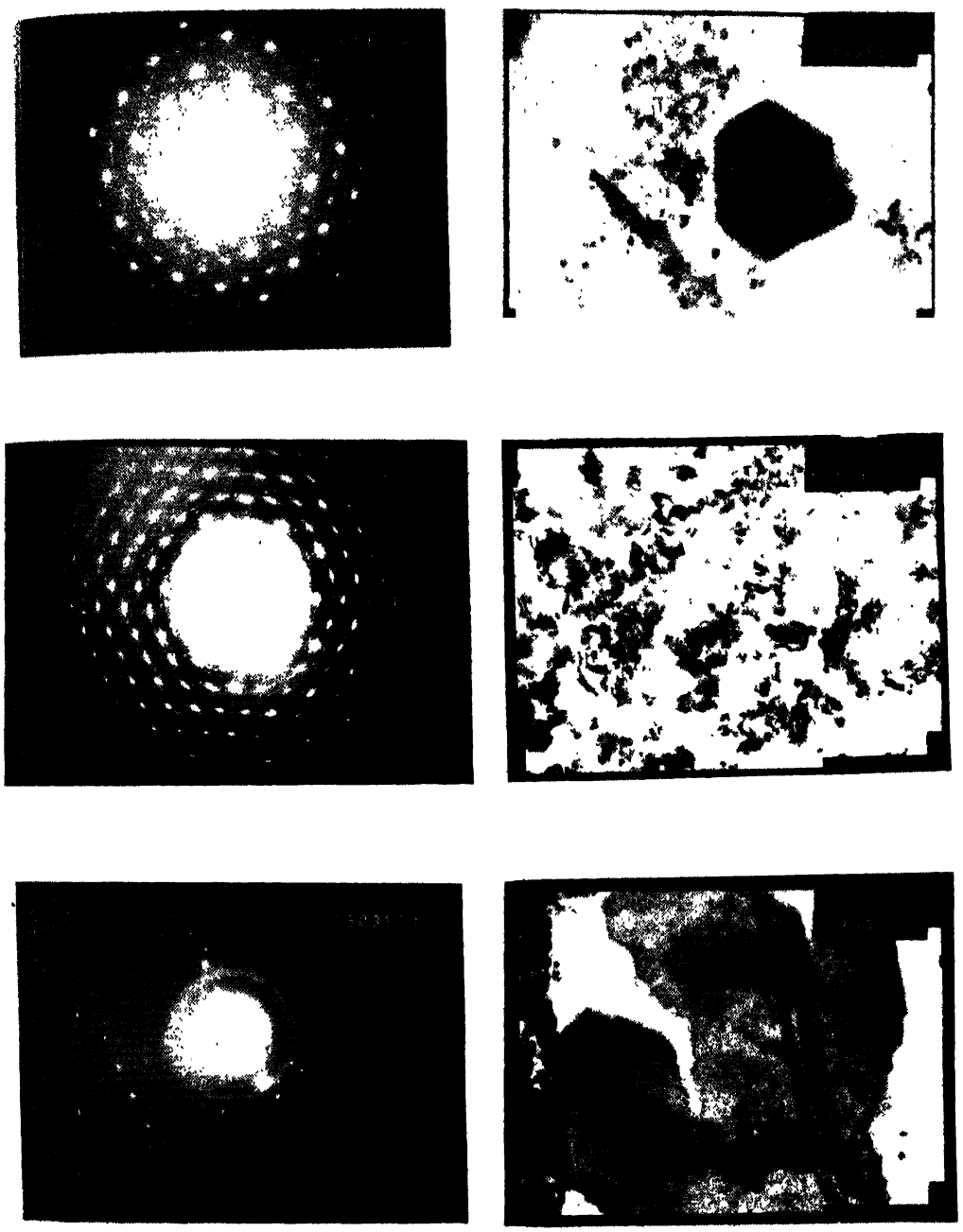

Fig. 3. Transmission Electron Diffraction Patterns and Micrographs for CdO (a) without any heat treatment and after (b) 400°C and (c) 800°C heat treatments for 36 hours.

loss of interstitial Cd atoms from different definite locations. The steps can be linked to the different potential barriers for different interstitial positions. Such excess of Cd as interstitials can, moreover, in case of a regular distribution of the interstitials, explain the extra x-ray lines in the as-supplied CdO. It is noted that this model of excess Cd being lost up to about 380°C is in agreement with our observation that the 400°C form can be concluded to be of nearly stoichiometric composition from the complete coincidence of its x-ray pattern (Fig.1) to the standard pattern. As the excess Cd atoms are primarily responsible for unaccounted lines in the pattern of as-supplied and 125°C forms, such excess lines are absent in 400 and 800 °C forms. The creation and extinction of metal excess defect is an important aspect in doping related [6] problems for CdO. The small downward slope of the mass loss with respect to temperature in the TGA pattern at higher temperatures is indicative of the gradual mass loss due to knocking off of oxygen from their lattice sites. Our last firing temperature of 800°C form is seen to be in the region of gradual oxygen loss, manifestation of which can be linked to the gradual decrease of intensity in the diffraction pattern.

The TEM patterns (Fig.3) throw light over the microstructure of the as-supplied (Fig.3a) and the heat-treated samples. In Fig.3a the non-homogeneous matrix contains some scattered hexagonal zones, one being shown in the micrograph. From this single crystal like hexagonal zone the diffraction pattern of Fig.3a was obtained. It is indeed a single crystal like pattern, unusual in a polycrystalline sample. The 400°C form (Fig.3b) is more homogeneous from microstructural as well as electron diffraction point of view. The 800°C form is still more uniform due to more possible means of thermal diffusion. But this form leaves some interesting unsolved issues like the amorphous hallow (Fig.3c) from some dense regions and a large semicircular scatter of points in the diffraction pattern. The loss of oxygen makes this form more populated with anion vacancy defects. This process can enhance electrical conduction by migration of defects. The 800°C firing indeed reduces the electrical resistance by three orders of magnitude.

4. Conclusion

The present work is a part of ongoing work on the material aspect of CdO. The 800°C form emerges as most interesting with many probable but unexplored applications. Also the detailed physics of its transport mechanism and resistivity change is quite interesting. This black form is a member of 1.1 to 1.3 eV compounds which should be explored for photochemical applications.

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